# VISCOELASTIC AND THERMOMECHANICAL BEHAVIOR OF HYSOL 141A RESIN

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Hysol 141A resin (an experimental epoxy resin for filament winding purposes) was investigated for its viscoelastic and thermomechanical behavior. The creep behavior of this resin increases strongly at slightly elevated temperature, which gives rise to some concern if this material were exposed to longterm loading. The resin modulus decreases rapidly above room temperature and the resin is virtually a rubber above 100°C,

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which makes the use of Hysol 141A highly questionable as a winding resin for rocket motor chambers.

NSWC/WOL/TR 75-4 27 January 1975

VISCOELASTIC AND THERMOMECHANICAL BEHAVIOR OF HYSOL 141A EPOXY RESIN

This report describes the results of using the time-temperature superposition principle to estimate the longterm creep behavior of an experimental epoxy resin (Hysol 141A) designed for filament winding of rocket motor chambers. Also determined was the change of resin modulus as function of temperature. The intent of the investigation was to obtain pertinent resin properties of this candidate resin for possible use in the TRIDENT rocket motor chambers. Since the production of ERLA 2256 (the best resin presently used for this purpose) has been discontinued, it is incumbent for the Navy to find a replacement for it. This report covers the effort from October 1973 to February 1974, funded by Stragetic Systems Project Office SSPO-77402/B1509001.

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By direction

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## INTRODUCTION

One of the components of the ERLA 2256 filament winding resin which was used for the C-3 rocket motor cases will no longer be produced. Therefore, it became necessary to find a substitute resin for C-4 TRIDENT motor cases. Hysol 141A (another commercial epoxy resin) gave good burst pressure results in six inch bottle tests and thus was considered a candidate resin to replace ERLA 2256. A preliminary evaluation of its thermomechanical behavior indicated a low glass transition temperature ( 65-84°C, depending on curing conditions) which is close enough to room temperature to cause concern about its creep behavior. The rocket chamber walls and skirt areas are not only simple pressure vessels but must also carry the weight of the missile while in storage. Therefore, a creep deformation particularly in the dome contour may severely change the calculated burst pressure. The objective of this investigation was to obtain information about the thermomechanical and viscoelastic properties of this new resin.

## EXPERIMENTAL

### Resin Cure

The two part resin was mixed in a ratio of 100 parts 141A and 20 parts 143B (curing agent) cast into molds of 1/8 and 1/2 inch thickness. The resin was then cured under the following conditions: It was held for one hour at 65°C then the temperature was raised to 120°C and kept at this temperature for two hours. The resin properties are given in Table 1.

### Creep Deformation Under Compressive Load

The cured resin was machined into 1/2 inch cubes and tested for creep deformation at constant load with a deformation testing machine as described by the ASTM test method D 621-64.

The measurements were run at various temperatures and at different loading conditions (415, 830, and 1630 psi). The testing machine was placed into an oven (with forced air circulation) with a temperature variation of not more than ± 1°C. These data were used to derive master curves for creep modulus, creep compliance and a 3-dimensional surface of deformation as function of time and load, and, by using the shift factor curve, also as function of temperature.

### Torsional Braid Analysis

The thermomechanical behavior of the resin was determined with a Torsional Braid Analyzer (Chemical Instrument Corporation). The glass braids were impregnated with the resin and cured under various conditions directly in the variable temperature chamber of the analyzer. The relative modulus versus temperature curves of the cured resins thus obtained were used to derive also absolute modulus curves by determining the absolute moduli (under compression) at two different temperatures. The relative rigidities at the same temperatures are in a one to one relationship with the absolute values, thus the logarithmic scale of relative rigidities ( $\frac{1}{p^2}$ ) can now be transformed into an absolute scale.

To determine the absolute moduli (under compressive loading) resin samples ( 1 x 0.5 x 0.5 inches) were tested at constant crosshead speed on an Instron Universal Testing machine at 23° and 160°C for Hysol 141A and at 23° and 200°C for ERLA 2256, respectively. Corrections due to the machine compliance were made by using a corresponding one inch steel bar.

## RESULTS AND DISCUSSION

Criteria for the resin selection of the C-4 motor chambers are based on delivered bottle burst pressure of Kevlar fiber reinforced pressure vessels, and on a number of fabrication parameters (see Table 2) which must be simultaneously met. Presently, there is no clear correlation between resin properties and high bottle burst pressures using Kevlar as a reinforcing fiber material.

Hysol 141A resin was one of the candidate resins under consideration as a replacement for the discontinued ERLA 2256 resin and was to be used for filament winding the C-4 TRIDENT rocket motor chambers. The properties of Hysol 141A and ERLA 2256 (see Table 1) are quite different from one another which effects their performance characteristics. For example, while the $T_g$ of ERLA 2256 is 152°C, that of Hysol 141A is only between 65-85°C (depending on cure), which means that one might expect a fairly high degree of creep at ambient or slightly elevated temperatures for this latter system. The major purpose of this investigation was to determine the creep behavior of the resin.

Also, since the strength of reinforced composites is, aside from certain fabrication parameters (for instance voids), dependent on resin modulus (see C. C. Chamis, reference 1) it was also desirable to obtain absolute modulus values of Hysol 141A as function of temperature.

### Deformation of Hysol 141A Resin Under Load; Creep Modulus and Creep Compliance*

In order to determine longterm creep behavior under compressive loading the time-temperature superposition principle was applied. The deformation under load was determined (according to ASTM D 621-64) at different loads and the results are given in Figures 1 through 3. These curves were used to derive master curves of creep deformation. An example is shown in Figure 4 which is the master curve for creep deformation at 22°C and 830 psi load. A three-dimensional projection of a master surface of percent deformation as a function of time and load is given in Figure 5, and, by using the shift factor curve, Figure 6, also as a function of temperature. (Thus the shift factor curve allows the determination of the creep behavior at any other temperature, at least between 10° and 80°C. This curve simply determines how much the master curve (or surface) has to be shifted parallel to the time axis (in the positive

* Originally it was planned to determine creep also on Hysol 141A - Kevlar composites. The experiments were stopped because Hysol 141A resin was rejected meanwhile as a viable resin candidate.

1. C. C. Chamis, M. P. Hanson, and T. T. Serafini, NASA TMX-68166 (1973).

or negative direction) depending on whether the temperature decreased or increased.

The creep deformation data of Figure 3 were used to derive the corresponding curves of creep modulus (and creep compliance), see Figure 7. By using the formula below:

$$E_{t\ (red)} = \frac{T_o\ \rho_o}{T\ \rho}\ E_t$$

$$E_t = \frac{\sigma}{\epsilon(t)}$$

where $E_{t\ (red)}$ is the reduced creep modulus as function of time; $T_o$ is the reference temperature, 295°F (22°C); T is the temperature at which the experiment was run (in °K); $\rho_o$ and $\rho$ are the resin densities at $T_o$ and T respectively; $E_t$ is the creep modulus at the time t; $\sigma$ is the constant load applied and $\epsilon(t)$ is the compressive deformation after time t. The reduced creep compliance $D_{t\ (red)}$ is the inverse of $E_{t\ (red)}$.

The master curve for creep modulus and creep compliance is shown in Figure 8.

A simple example shall illustrate how one may use the master curve to predict deformation under load at temperatures other than 22°C (the reference temperature).

Using Figure 4, we can see that at room temperature (22°C) and at a constant load of 830 psi the polymer should deform eight percent over a period of 100 years. If we want to know how long it would take for the same deformation at 32°C, we use the shift factor curve (Figure 6) and find that a 10°C rise in temperature corresponds to a shift of the master curve two decades to the left i.e. negative direction of the time axis. Thus the deformation is reached already after one year. If the temperature is raised to 42°C, this deformation occurs within three and one-half days. Let us assume the cure temperature of the propellant were 74°C and the applied load were the same, than we would find that this deformation occurs within one second. (It should be noted, however, that this applied to the resin only. The deformation of a composite depends on the geometry i.e. the fiber direction so that shear and compressive deformations will have to be determined. An example for shear creep deformation has been described by D. F. Sims and J. C. Halpin, reference 2.)

Change of Modulus versus Temperature

Torsional braid analysis (TBA) can be used to determine in a very simple way the change of Young's modulus of polymeric materials over a wide range of temperature above and below $T_g$.

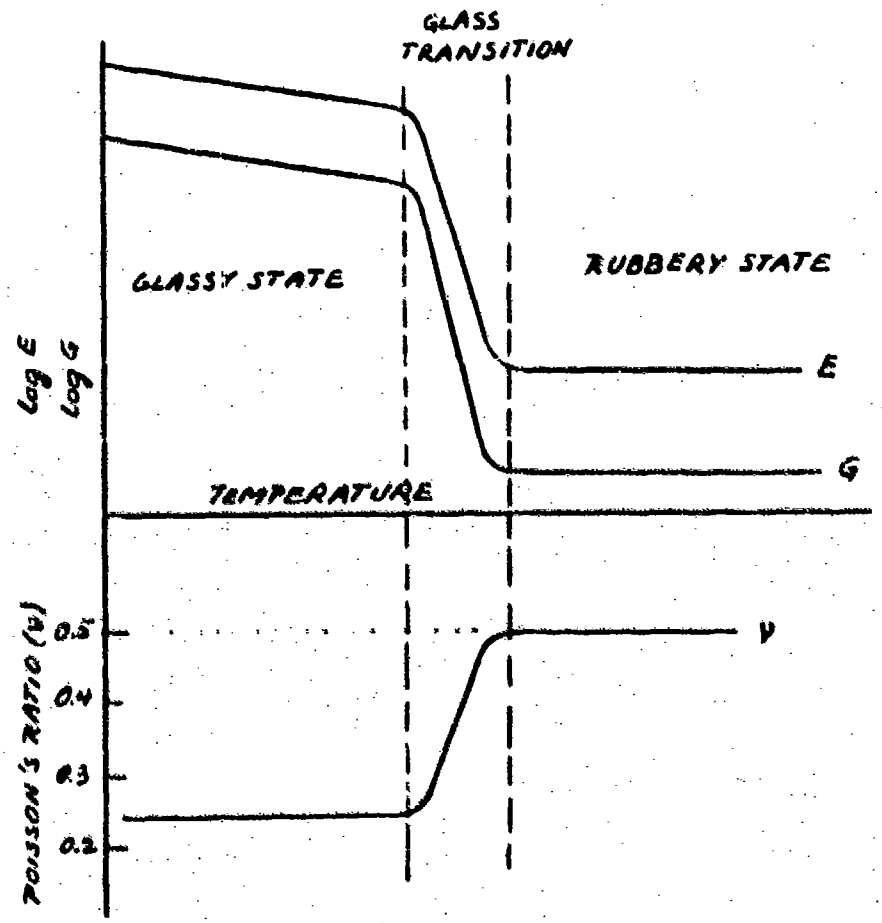
From torsional braid analysis of polymeric materials one does not obtain directly the shear modulus (since the geometry of the braid is poorly defined).

2. D. F. Sims and J. C. Halpin, Composite Materials: Testing and Design. ASTM Special Technical Publication 546 (1974), p. 46.

However, one obtains a relative shear modulus ($\frac{1}{p^2}$, where p is the period of the torsional motion).

This relative rigidity curve of log $\frac{1}{p^2}$ versus temperature is in a one to one relationship with the absolute curve of shear modulus log G, which in turn is related to the Young's modulus by the expression $E = 2G(1 + \upsilon)$ where $\upsilon$ is the Poisson's ratio. Thus, by changing the logarithmic scale the relative rigidity curve can be transformed into an absolute modulus curve of G or E. The scale for G is defined if two points of G are determined by methods giving absolute G values (preferably above and below $T_g$). In order to determine E from G one has to know the Poisson's ratio ($\upsilon$) as function of temperature.

Above and below the glass transition the dependence of $\upsilon$ on temperature is small and $E \ll G$ i. e. a parallel shift on the logarithmic modulus temperature curve (see figure below).




By determining two absolute values of E (above and below $T_g$) one can also get an absolute scale of log E which, however, is not the same as that for log G since the change of Poisson's ratio is included. Or inversely, by determining the TBA curve, two values each of E and G (both above and below $T_g$), one may estimate the change of Poisson's ratio in the transition region.

This method was used to obtain the absolute modulus-temperature curve of Hysol 141A and ERLA 2256. The Instron machine tested samples were cured under the same conditions as the TBA specimens.

Figures 9 and 10 show the thermomechanical behavior of the resins Hysol 141A and ERLA 2256 as determined by TBA. (The glass transition temperatures $T_g$ were defined as the maxima of the mechanical damping curve. It should be noted that $T_g$'s thus defined may differ somewhat from those determined by thermal expansion coefficients or by scanning calorimetry.) The corresponding absolute Young's modulus curve, determined as described above, are shown in Figures 11 and 12.

## CONCLUSIONS

1. The resin Hysol 141A has a fairly low glass transition temperature (65-85°C depending on curing).

2. The resin modulus decreases rapidly with increasing temperature and reaches a rubbery state at about 100°C.

3. The creep at room temperature is not excessive. However, it increases rapidly at slightly elevated temperatures.

## RECOMMENDATIONS

The resin Hysol 141A should not be used for C-4 rocket motor cases unless it has been assured that:

a. The low $T_g$ does not lead to excessive deformations of the motor chambers during propellant cure,

b. That Kevlar composites will not creep significantly under rocket storage conditions, and

c. That the calculated chamber pressure is maintained at the elevated temperature during flight conditions.

## ACKNOWLEDGEMENT

We thank Mr. H. Matheus who carried out the deformation measurements.

Table 1

Comparison of Resin Properties of Hysol 1h1A and ERLA 2256

| Resin Properties | Hysol 1h1A/1h3B | ERLA 2256/TONOX 60h0 |
|---|---|---|
| Density | 1.197 | 1.225 |
| Glass Transition Temperature, °C | 65 | 152 |
| Tensile Strength, psi x $10^3$ | 4 | 14.8 |
| Tensile Strength, psi x $10^3$ after 28 days 97°C, 95% RH | 2.5 | 11.8 |
| % loss in Tensile Strength | 37.5 | 20.3 |
| Modulus, psi x $10^5$ | 1.917 | 4.895 |
| Modulus after 28 days 97°C, 95%, psi x $10^5$ | 1.194 | 4.141 |
| % loss in Modulus | 34.3 | 15.4 |
| % Elongation | 59 | 7.3 |
| % Elongation after 28 days 97°C, 95% RH | 26 | 4.8 |
| % loss in Elongation | 55 | 34.2 |
| Hardness | 80 (Shore D) | 118 (Rockwell M) |
| Hardness after 28 days 97°C, 95% RH | 78 (Shore D) | 108 (Rockwell M) |
| % Water Absorption after 28 days 97°C, 95% RH | 3.92 | 4.05 |

Table 2

Resin Criteria for the C-4 Chamber

1. Initial viscosity < 1500 cps
2. Long pot life at 25°C
3. Good fiber wetting properties
4. Maximum cure temperature ≤ 150°C
5. Reactive to microwave curing
6. Low shrinkage after curing
7. Heat distortion temperature > 100°C
8. Low water absorption
9. Low density
10. High uniaxial tensile and modulus properties
11. High elongation (> 6%)
12. Interlaminar shear strength
13. Pass EPA and OSHA regulations

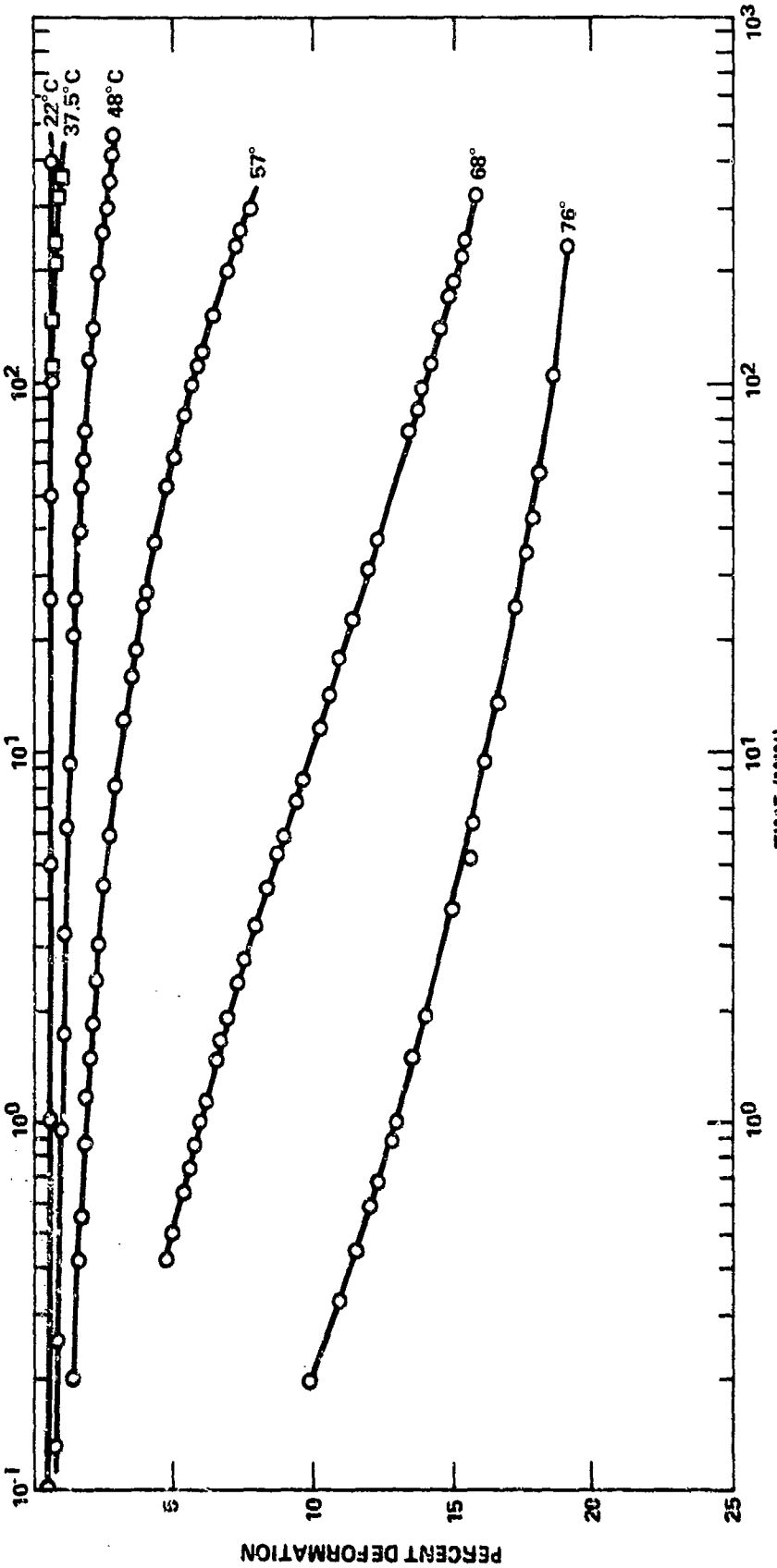



FIG. 1 CREEP DEFORMATION OF HYSOL 141A EPOXY RESIN UNDER CONSTANT LOAD (415 PSI), AT VARIOUS TEMPERATURES

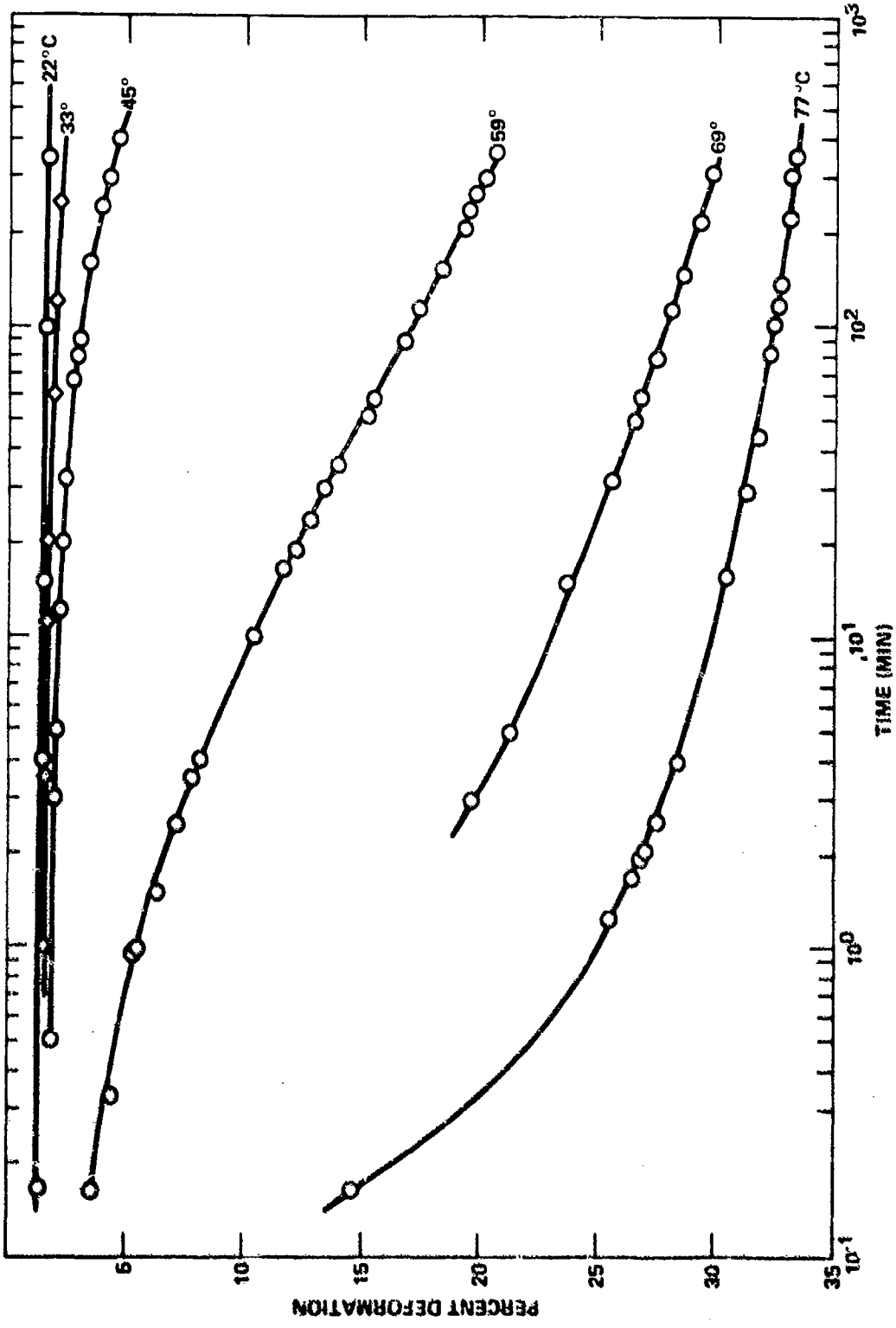



FIG. 2 CREEP DEFORMATION OF HYSOL 141A EPOXY RESIN UNDER CONSTANT LOAD (830 PSI), AT VARIOUS TEMPERATURES

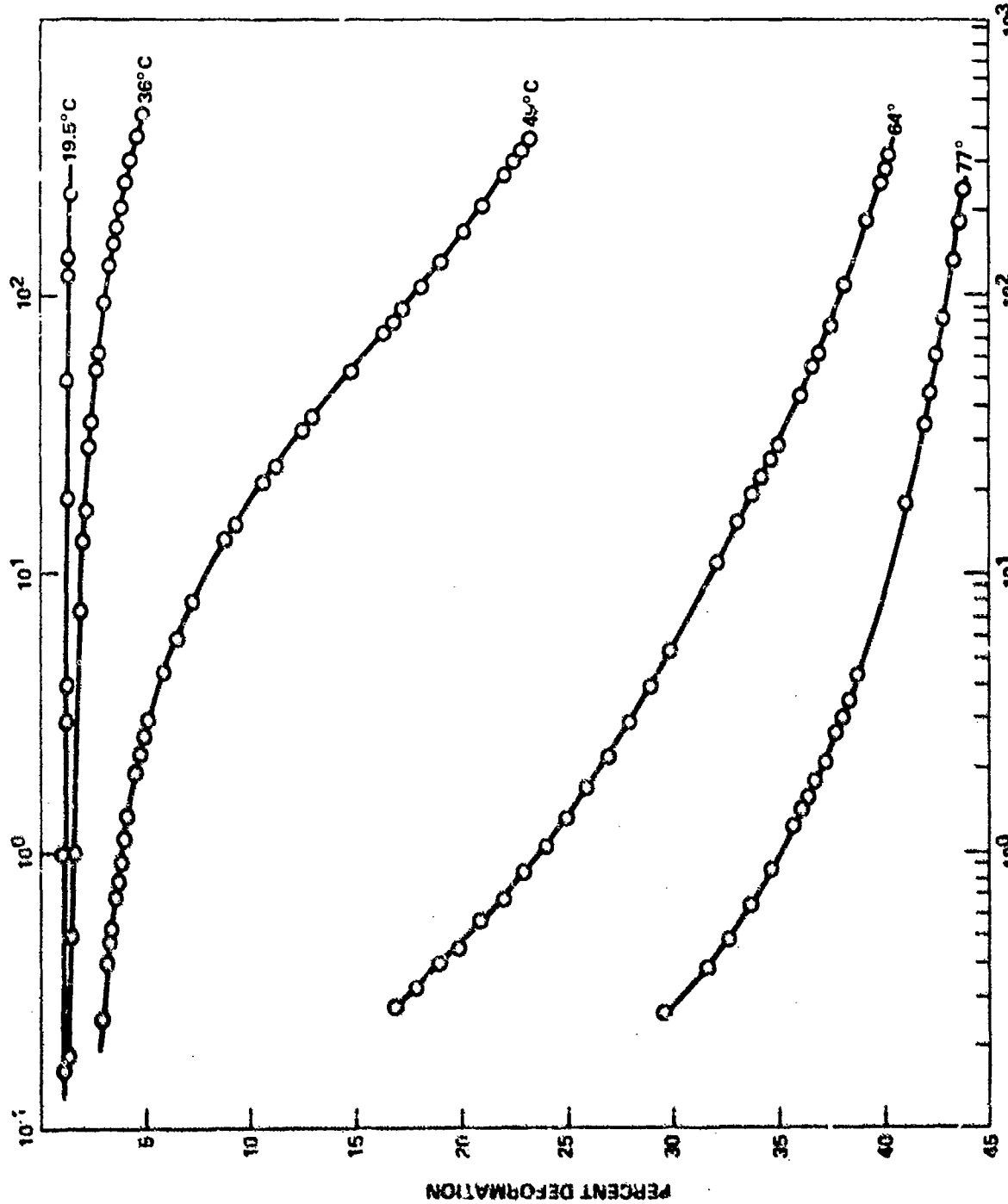



FIG. 3 CREEP DEFORMATION OF HYSOL 141A EPOXY RESIN UNDER CONSTANT LOAD (1638 PSI) AT VARIOUS TEMPERATURES

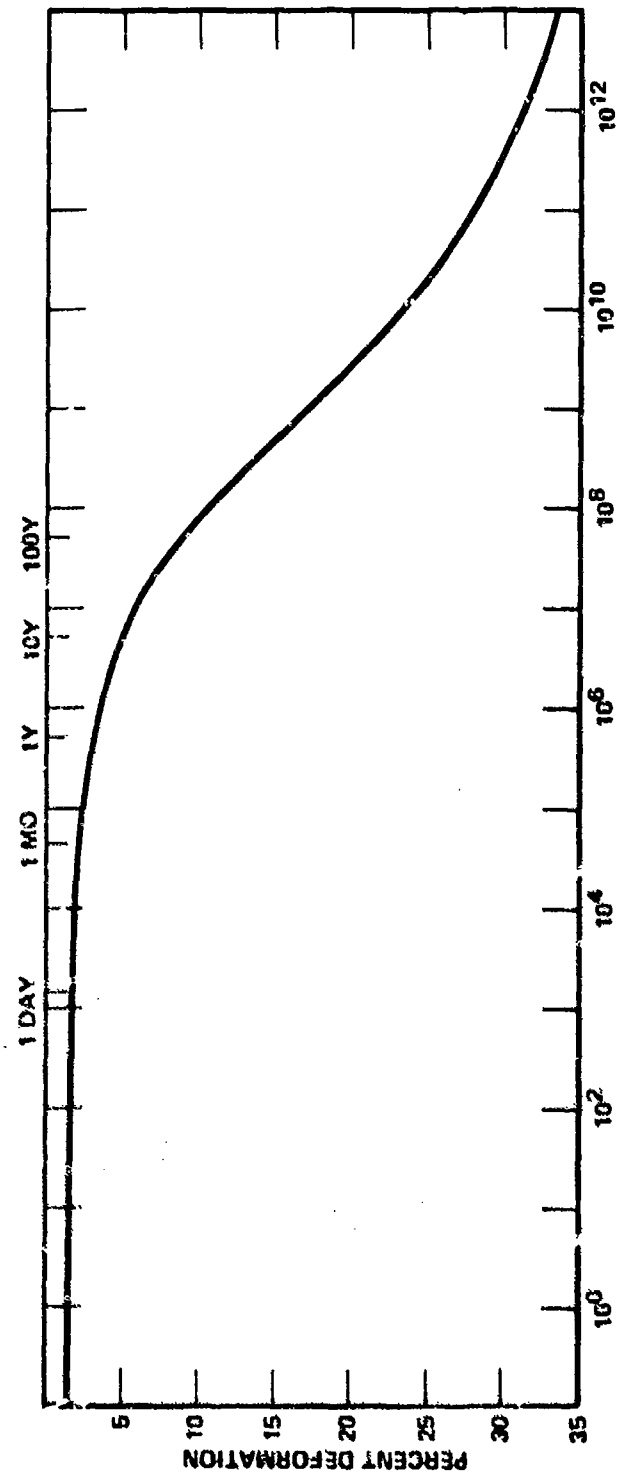



FIG. 4 MASTER CURVE FOR CREEP DEFORMATION OF HYSOL 141A EPOXY RESIN (AT 830 PSI, REFERENCE TEMP. 22°C)

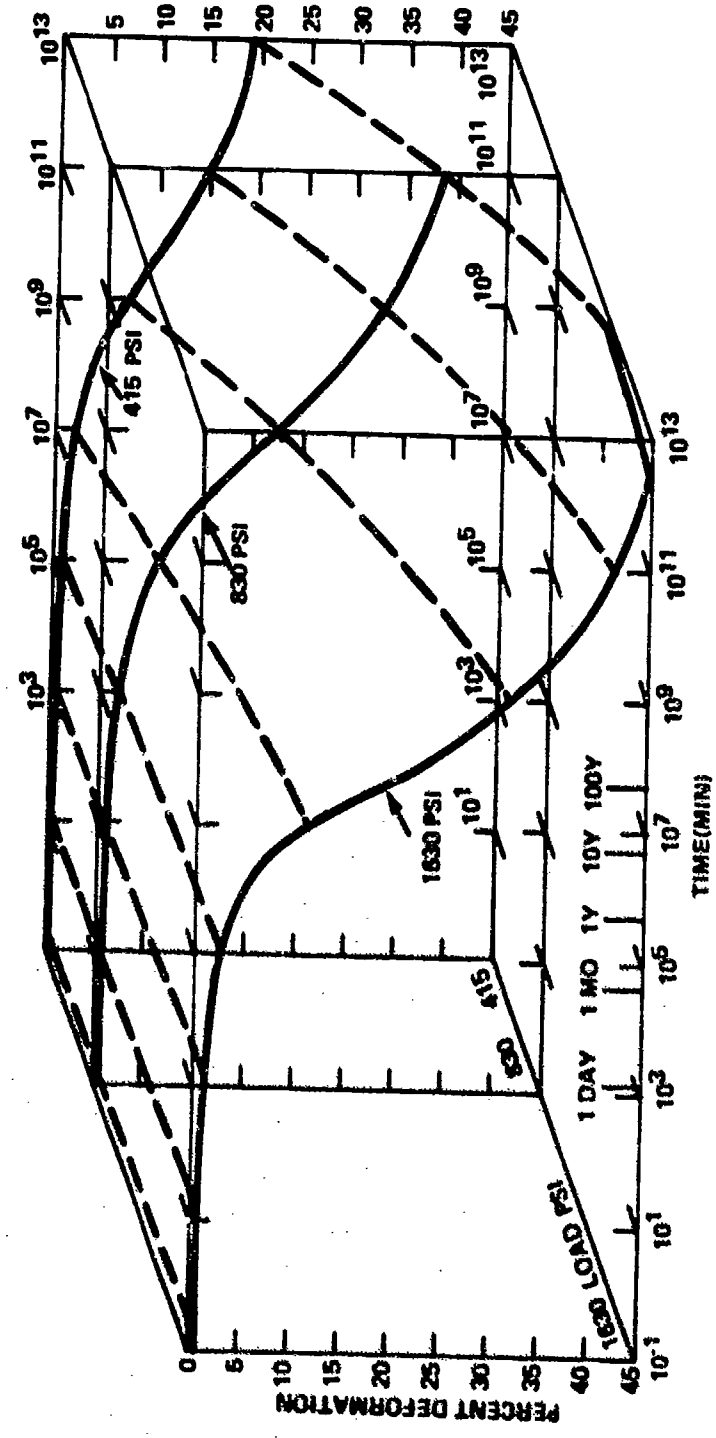



FIG. 5 MASTER SURFACE FOR CREEP DEFORMATION OF HYSOL 141A EPOXY RESIN AS FUNCTION OF LOAD AND TIME. (REFERENCE TEMP. 22°C).

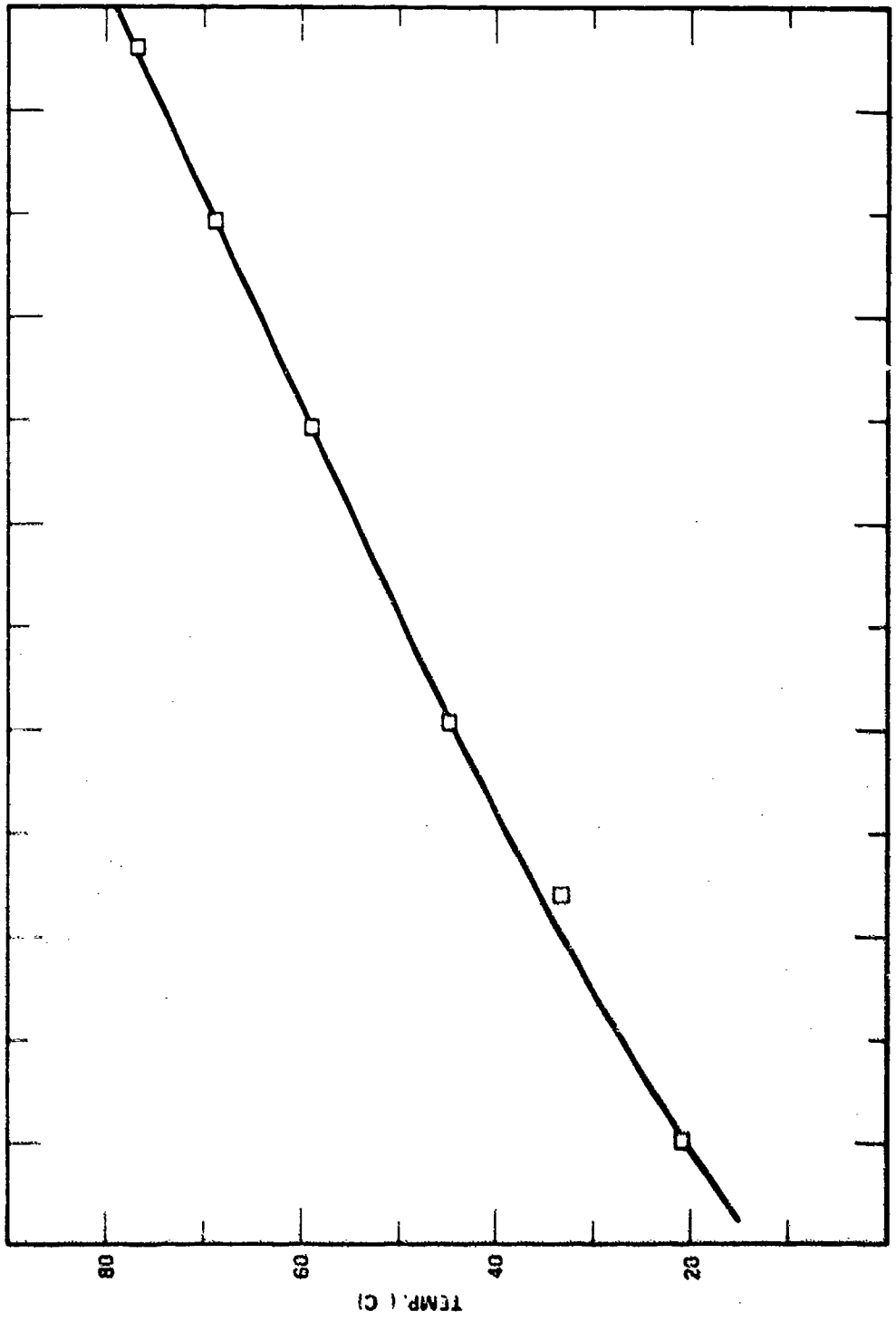



FIG. 6 SHIFT FACTOR VS. TEMPERATURE FOR HYSOL 141A

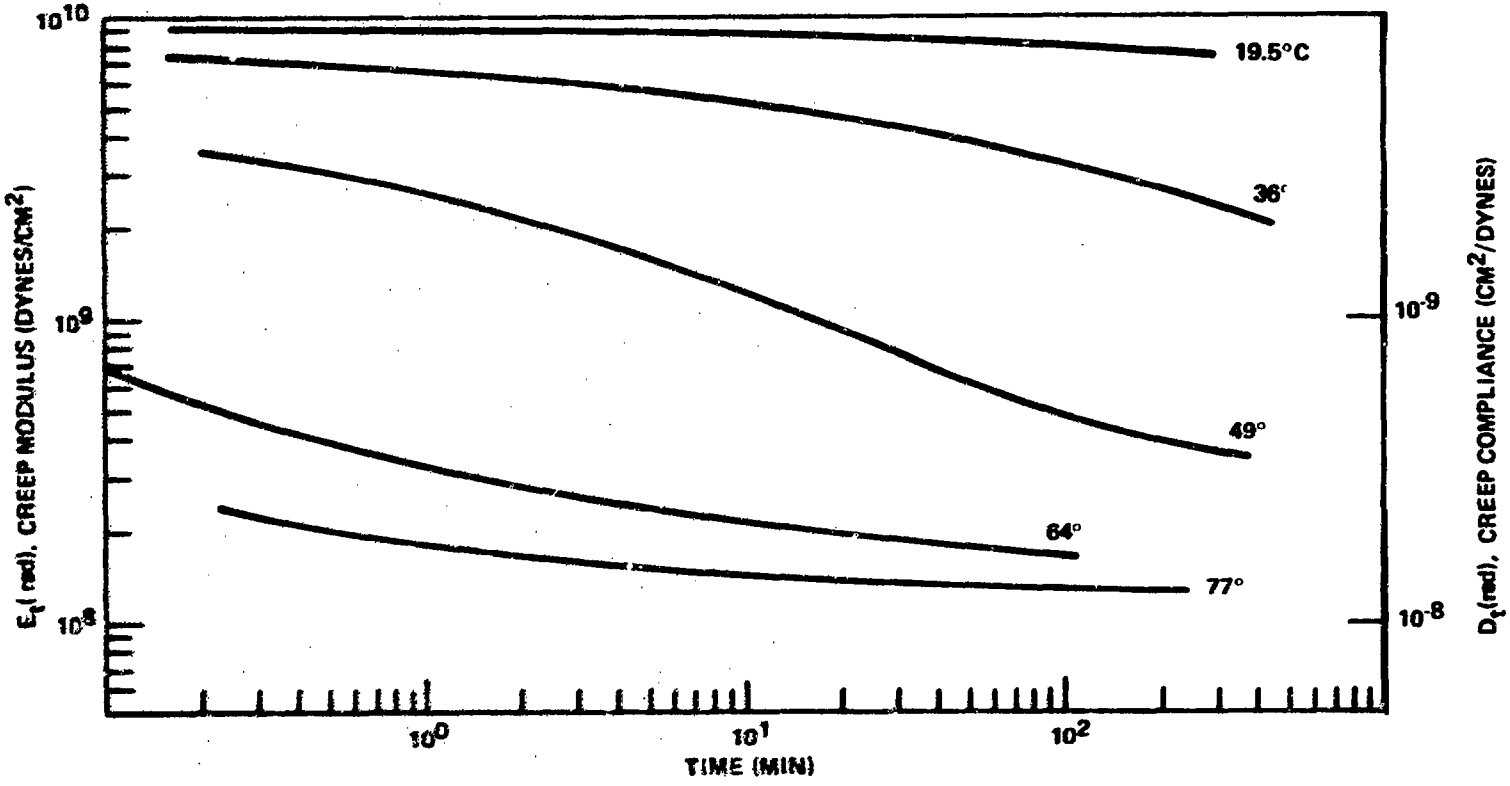



FIG. 7 CREEP MODULUS AND CREEP COMPLIANCE FOR HYSOL 141A EPOXY RESIN AT VARIOUS TEMPERATURES.

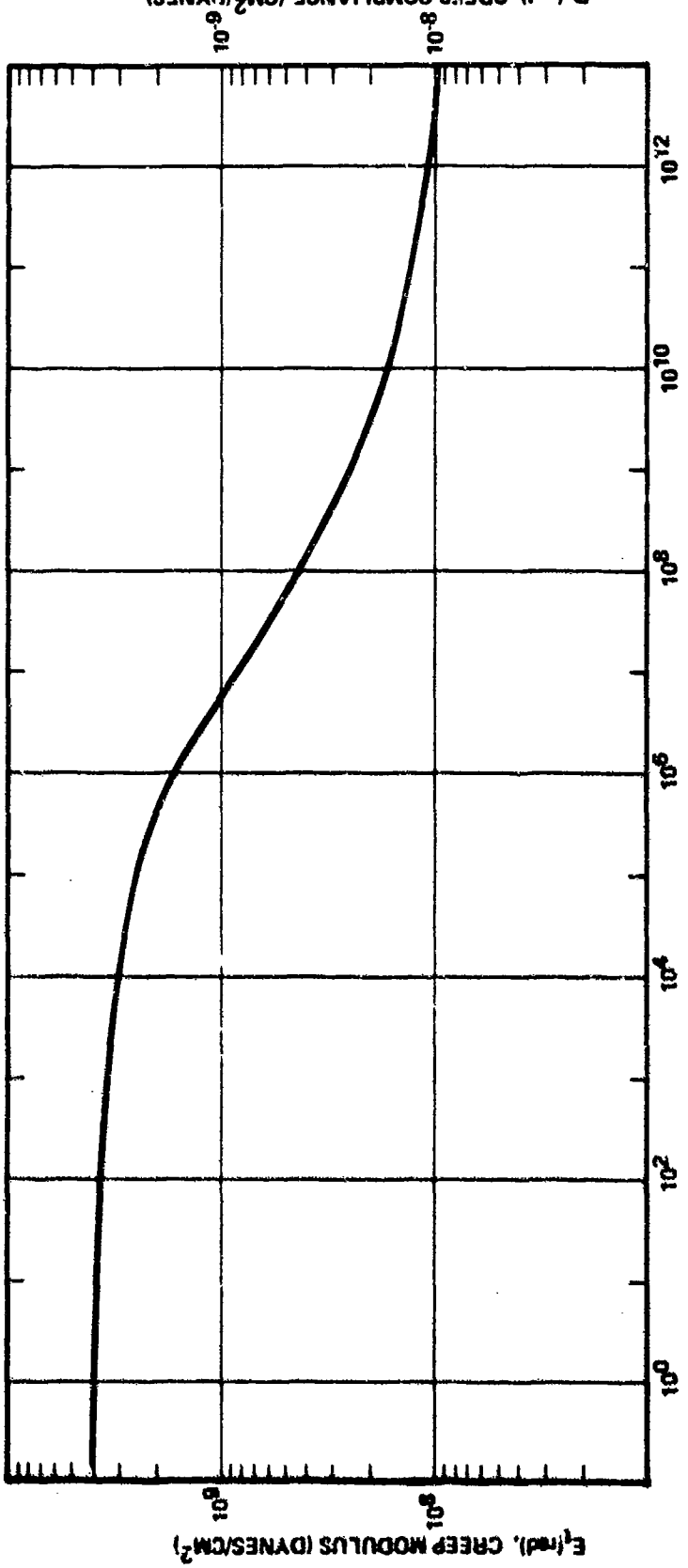



FIG. 8 MASTER CURVE FOR CREEP MODULUS AND CREEP COMPLIANCE OF HYSOL 141 A (REF. TEMP. 22°C)

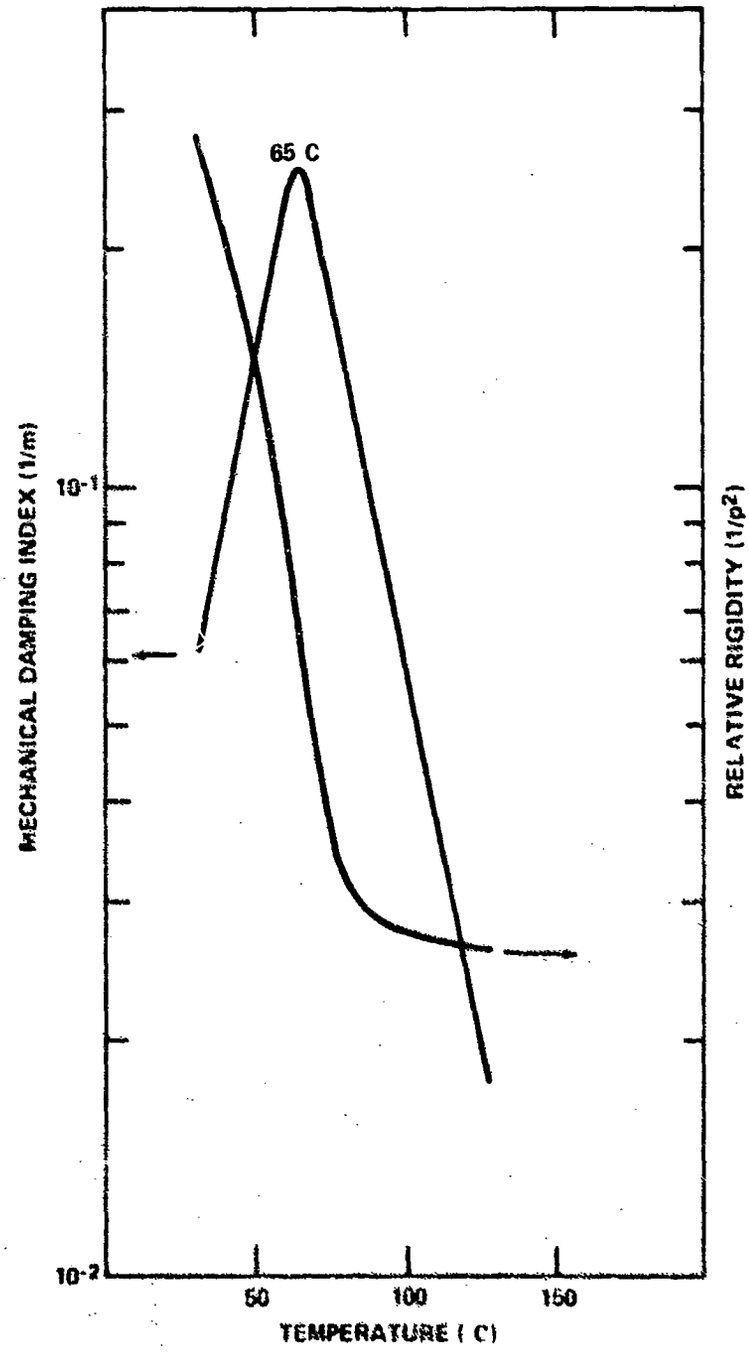



FIG. 6 THERMOMECHANICAL BEHAVIOR OF HYSOL 141A EPOXY RESIN

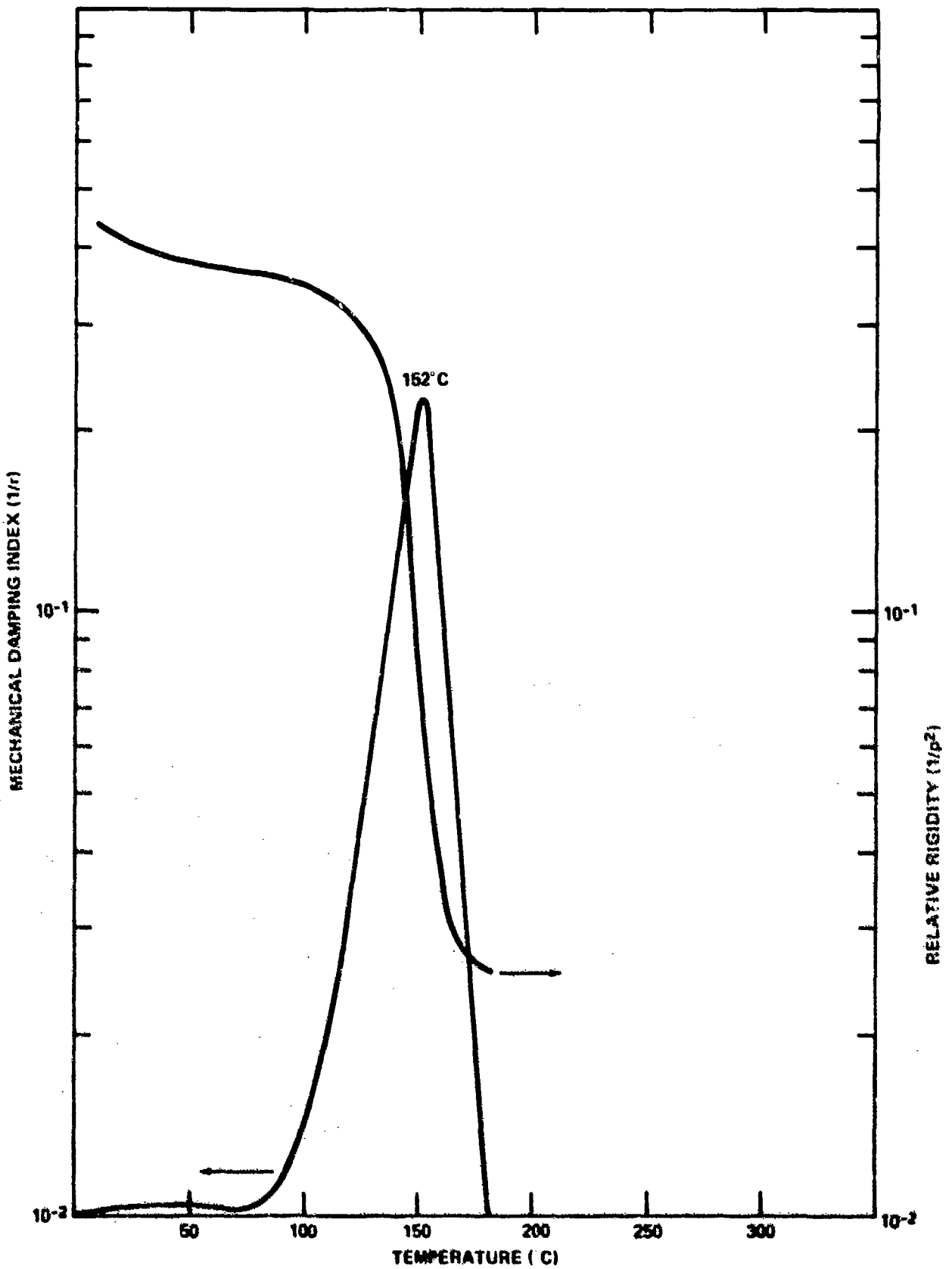



FIG. 10 THERMOMECHANICAL BEHAVIOR OF ERLA 2256/TONOX (AFTER 5 HOURS POST CURE AT 160° C)

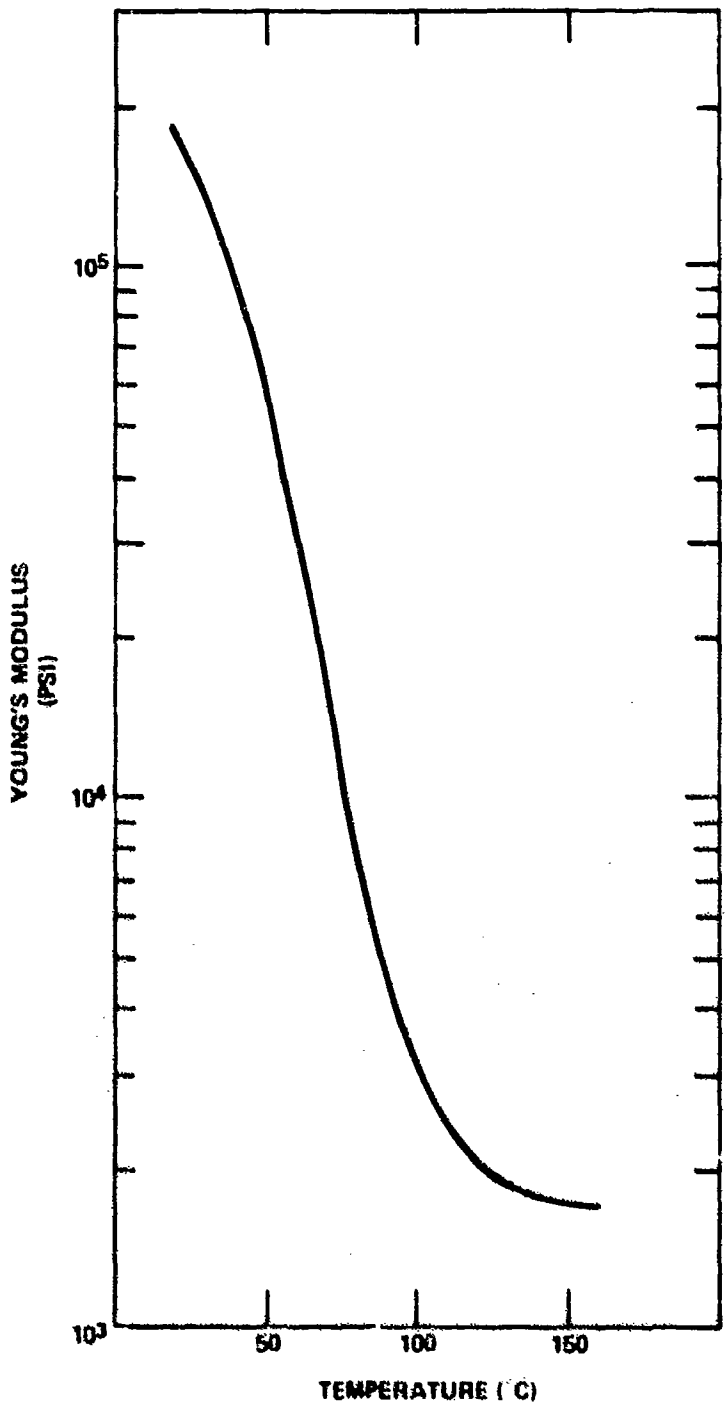



FIG. 11 YOUNG'S MODULUS AS FUNCTION OF TEMPERATURE
RESIN: HYSOL 141A

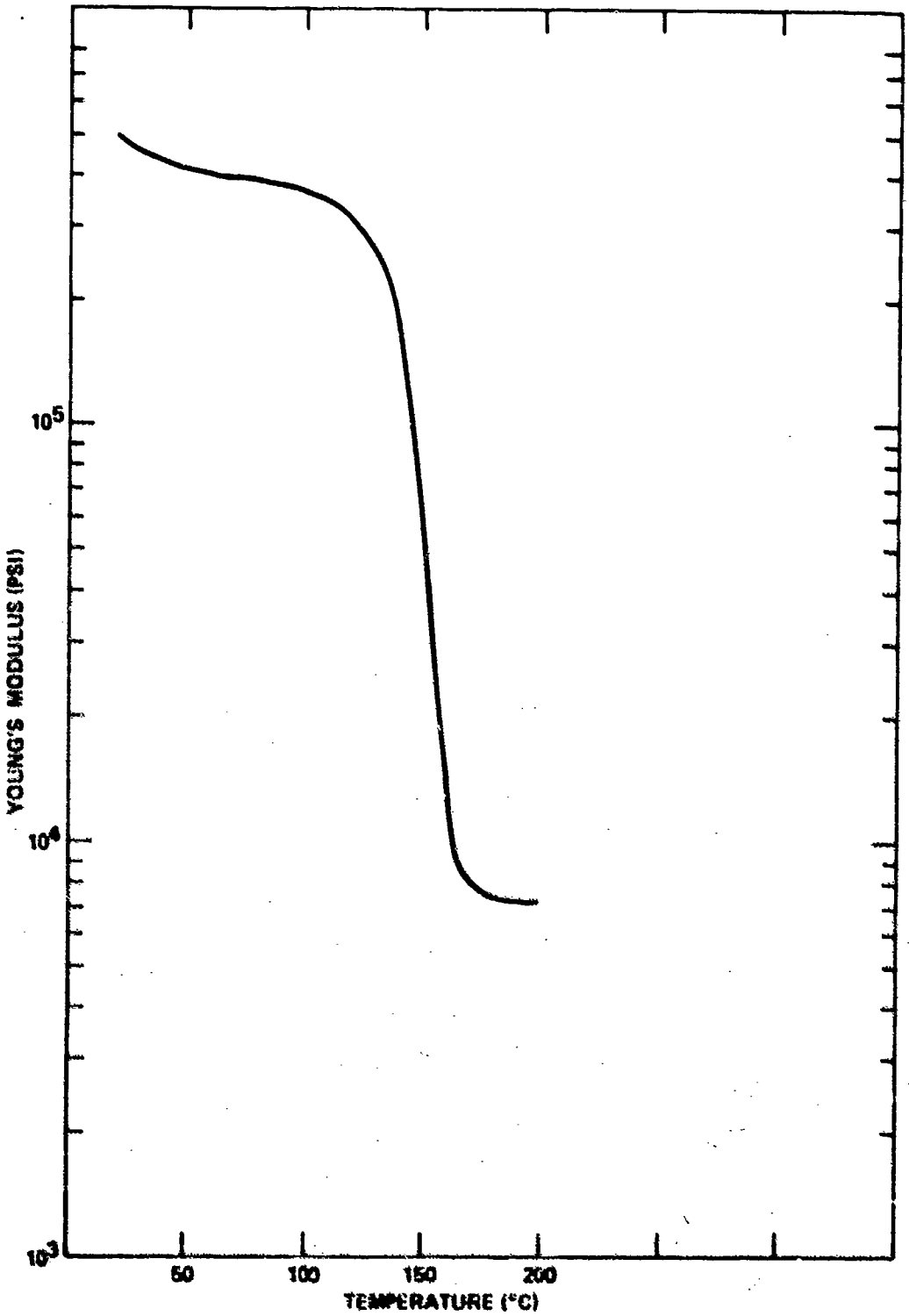



FIG. 12 YOUNG'S MODULUS AS FUNCTION OF TEMPERATURE.
RESIN: ERLA 2256/TONOX 6040 (AFTER 5 HR5 POST CURE AT 150°C)